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(71)Applicant : NICHIA CHEM IND LTD

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(72)Inventor : MAKINO KENYA

**(54) POLYMERIC HOLE TRANSPORT MATERIAL, AND ORGANIC
ELECTROLUMINESCENT ELEMENT USING THE SAME**

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a thin film layer used for an organic electroluminescent element and the like, and to obtain the organic electroluminescent element with high luminous efficiency of which, a hole transport layer with large area can be easily manufactured.

SOLUTION: The polymeric hole transport material is composed of a copolymer of vinyl monomer having substituent, and acrylate or methacrylate having unsaturated group. The substituent is at least one group chosen from carbazole group, carbazole derivative group, triphenylamine, and triphenylamine derivative group. It is preferable that the unsaturated group is aliphatic unsaturated hydrocarbon residue with 2 to 20 carbons, and that the distribution ratio of the vinyl monomer having substituent to the total monomer of the copolymer ranges between 0.5 to 0.9, and that the degree of polymerization of the copolymer ranges between 10 and 1,000. The organic electroluminescent element has more than one layer of organic thin film having the light emitting layer as a minimum between the positive electrode and the negative electrode, and the light emitting layer and/or the organic thin film contacting with the light emitting layer includes this polymeric hole transport material.

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TITLE: Polymeric hole transportation material for
organic electroluminescent materials, comprises
copolymer of vinyl monomer having substituent, and acrylate
or methacrylic ester having unsaturated group

PATENT-ASSIGNEE: NICHIA KAGAKU KOGYO KK[NICHN]

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PATENT-FAMILY:

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APPLICATION-DATA:

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H05B033/14 , H05B033/22

ABSTRACTED-PUB-NO: JP2003142272A

BASIC-ABSTRACT:

NOVELTY - The polymeric hole transportation material comprises a
copolymer of a
vinyl monomer having a substituent, and acrylate or methacrylic ester
having an
unsaturated group. The substituent is carbazole (derivative) and/or
triphenylamine (derivative).

DETAILED DESCRIPTION - An INDEPENDENT CLAIM is also included for
organic
electroluminescent material.

USE - For organic electroluminescent material (claimed).

ADVANTAGE - The polymeric hole transportation material provides organic electroluminescent materials having excellent luminous efficiency, without causing substrate dissolution. The filming method is economized, and workability is improved.

CHOSEN-DRAWING: Dwg.0/0

DERWENT-CLASS: A14 A85 L03 T04 U11

CPI-CODES: A04-D06; A04-D09; A04-F06E; A12-E11C; L03-D01D;

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【特許請求の範囲】

【請求項1】 置換基を有するビニルモノマーと、不飽和基を有するアクリル酸エステル又はメタクリル酸エステルとの共重合体からなり、該置換基はカルバゾール基、カルバゾール誘導体基、トリフェニルアミン基、及びトリフェニルアミン誘導体基の群から選ばれる少なくとも1種であることを特徴とする高分子正孔輸送材。

【請求項2】 前記不飽和基は、炭素数が2乃至20である脂肪族不飽和炭化水素残基であることを特徴とする請求項1に記載の高分子正孔輸送材。

【請求項3】 前記共重合体において、前記置換基を有するビニルモノマーの構成モノマー全体に対する構成比率は0.5乃至0.9の範囲であることを特徴とする請求項1乃至2に記載の高分子正孔輸送材。

【請求項4】 前記共重合体の重合度は10乃至100000の範囲であることを特徴とする請求項1乃至3に記載の高分子輸送材。

【請求項5】 対向する陽極と陰極との間に、少なくとも発光層を有する1層以上の有機薄膜からなる層を具備する有機電界発光素子であって、該発光層及び/又は該発光層に接する有機薄膜は、請求項1乃至4に記載の高分子正孔輸送材を含むことを特徴とする有機電界発光素子。

【請求項6】 対向する陽極と陰極との間に、有機薄膜からなる正孔輸送層及び発光層を具備する有機電界発光素子において、該正孔輸送層は、請求項1乃至4に記載の高分子正孔輸送材からなる薄膜を光反応により溶媒不溶化されたものであることを特徴とする請求項5に記載の有機電界発光素子。

【請求項7】 前記正孔輸送層は、所定の開口パターンを有するマスクで覆われ光照射により選択的に溶媒不溶化された部分と、光照射されなかった溶媒不溶化されない部分が形成され、該溶媒不溶化されない部分を溶剤によりエッチング除去された結果、該マスクの開口パターン形状が形成されてなることを特徴とする請求項6に記載の有機電界発光素子。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、複数の有機薄膜を積層可能な高分子正孔輸送材及びそれを用いた有機電界発光素子に関する。

【0002】

【従来の技術】電界発光素子には、無機材料からなる無機電界発光素子と、有機材料からなる有機電界発光素子がある。近年、低電圧で高輝度の発光が得られるという理由から有機電界発光素子が注目を集めている。

【0003】一般に有機電界発光素子は、インジウムスズ酸化物(ITO)等の陽極材料の薄膜を蒸着したガラス板上に、正孔輸送層、発光層等の有機薄膜層を形成し、さらにその上に陰極材料の薄膜を形成して作られ

る。正孔輸送層、発光層等の有機薄膜層形成に使用する材料は、低分子材料と高分子材料に大別される。低分子材料と高分子材料の違いは、その製膜方法による。たとえばアルミニウムトリスキノリノール(以下Alq3と略す)に代表される低分子材料を用いた場合、薄膜を製作するには真空蒸着が必要であり作業効率が悪い。その点、高分子材料を用いた場合、その溶液からスピンコート法、バーコート法、ディップコート法、フローコート法、スクリーン印刷法、インクジェットプリンティング法などの簡便な塗布方式で製膜できる。さらに、このような塗布方式による製膜方法は、真空蒸着法に対し、大面積化、生産コストの低下、加工性などの点で非常に有利である。

【0004】有機電界発光素子用の正孔輸送材、発光材として種々の高分子材料が開発されている。たとえば正孔輸送材としてはトリフェニルアミンの誘導体で高分子化した材料(K. Ogino, H. Sato, et al, Macromol. Rapid commun. 20, 103-106 (1999))などが知られている。高分子発光材としては、ポリフルオレン系のポリマー(M. Inbasekaran, E. Woo, et al, Synth. metals, 111-112, 397 (2000), I. S. Millard, ibid. 111-112, 119 (2000))などが知られている。またポリビニルカルバゾールは正孔輸送材、発光材の両方に研究されている(J. Kido, et al, Appl. Phys. Lett. 63, 2627, (1993))。これらの高分子系の正孔輸送材、発光材を溶液とし、スピンコートなどの上記方法にて製膜し、さらに同様の方法にて次層を製膜し積層を試みると、先に製膜した薄膜が後から製膜しようとするポリマー溶液の溶媒に溶解し、きれいな多層の積層薄膜ができない。

【0005】ポリフェニレンビニレン(以下PPVと略)の様な長い共役系を持つ重合体がよく知られている。しかしながら、高分子材料の中でもPPVは溶媒に不溶であるため、そのまま塗布することができない。このような高分子材料の中でも溶媒に不溶の場合は、前駆体を合成し、スピンコート法等で薄膜にしてから加熱処理により目的物へ変換しなければならず、作業工程が複雑になる。

【0006】

【発明が解決しようとする課題】上記のように、薄膜化が容易な有機電界発光素子用の高分子材料の研究が盛んになされているが、満足なものとは得られていない。

【0007】高分子の不飽和基を有する正孔輸送材料薄膜に、可視光、紫外線などの光を照射することにより薄膜を硬化、不溶化し、その上に同材料または異種材料の薄膜を積層する材料が得られれば有機電界発光素子の製造が非常に簡単になり、しかも大面積素子が容易にでき

ることになり、産業上非常に有効な手段になる。従って、発明は上述した問題を解決することを課題として成されたものである。

【0008】

【課題を解決するための手段】本発明の高分子正孔輸送材は、

(1) 請求項1に記載するように、置換基を有するビニルモノマーと、不飽和基を有するアクリル酸エステル又はメタクリル酸エステルとの共重合体からなり、該置換基はカルバゾール基、カルバゾール誘導体基、トリフェニルアミン基、及びトリフェニルアミン誘導体基の群から選ばれる少なくとも1種であることを特徴とする。

(2) 請求項2に記載するように、(1)において不飽和基は、炭素数が2乃至20である脂肪族不飽和炭化水素残基であることが好ましい。

(3) 請求項3に記載するように、(1)乃至(2)における共重合体において、前記置換基を有するビニルモノマーの構成モノマー全体に対する構成比率は0.5乃至0.9の範囲であることが好ましい。

(4) 請求項4に記載するように、(1)乃至(3)における共重合体の重合度は10乃至100000の範囲であることが好ましい。

【0009】また、本発明の有機電解発光素子は、

(5) 請求項5に記載するように、陽極と陰極との間に、少なくとも発光層を有する1層以上の有機薄膜からなる層を具備する有機電解発光素子であって、該発光層又は該発光層に接する有機薄膜は、(1)乃至(4)に記載の高分子正孔輸送材を含むことを特徴とする。

(6) 請求項6に記載するように、陽極と陰極との間に、有機薄膜からなる正孔輸送層及び発光層を具備する有機電界発光素子において、該正孔輸送層は、(1)乃至(4)に記載の高分子正孔輸送材からなる薄膜を光反応により溶媒不溶化されたものが好ましく適用される。

(7) 請求項7に記載するように、(6)における正孔輸送層は、所定の開口パターンを有するマスクで覆い光照射により選択的に溶媒不溶化された部分と、光照射されなかった溶媒不溶化されない部分が形成され、該溶媒不溶化されない部分を溶剤によりエッチング除去された結果、該マスクの開口パターン形状が形成されてなるものが好ましく適用される。

【0010】このように構成することにより、本発明に係る有機電界発光素子は、その材料の製膜時に真空蒸着法を使用することなく、スピンコート法、ディップコート法、インクジェットプリンティング法などの簡便な塗布方式で製膜することができる。

【0011】

【発明の実施の形態】以下、本発明を詳細に説明する。本発明に使用する置換基を有するビニルモノマーは、その置換基は正孔輸送能を有することが必要であり、そのような置換基として、カルバゾール基、カルバゾール誘

導体基、トリフェニルアミン基、及びトリフェニルアミン誘導体基の群から選ばれる少なくとも1種が使用できる。

【0012】より具体的には、カルバゾール系として、カルバゾール基と、アルキル置換カルバゾール基を有するビニルモノマーが好ましく使用できる。トリフェニルアミン系として、トリフェニルアミン、N,N'-ビス(3-メチルフェニル)-N,N'-ジフェニル[1,1'-ビフェニル]-4,4'-ジアミン(TPD)、4,4',4''-トリス[1-ナフチル(フェニル)アミノ]トリフェニルアミン(1-TNATA)、4,4',4''-トリス[2-ナフチル(フェニル)アミノ]トリフェニルアミン(2-TNATA)、4,4',4''-トリス[ビフェニル-4-イル(3-メチルフェニル)アミノ]トリフェニルアミン(p-PMTDAT A)、4,4',4''-トリス[9,9-ジメチルフルオレン-2-イル(フェニル)アミノ]トリフェニルアミン(TFATA)、4,4',4''-トリス(N-カルバゾイル)トリフェニルアミン(TCT A)、1,3,5-トリス-[N-(4-ジフェニルアミノフェニル)フェニルアミノ]ベンゼン(p-DPA-TDAB)、1,3,5-トリス[4-(メチルフェニル(フェニル)アミノ)フェニル]ベンゼン(MTDAPB)、N,N'-ジ(ビフェニル-4-イル)-N,N'-ジフェニル[1,1'-ビフェニル]-4,4'-ジアミン(p-BPD)、N,N'-ビス(9,9-ジメチルフルオレン-2-イル)-N,N'-ジフェニルフルオレン-2,7-ジアミン(PFFA)、N,N,N',N'-テトラキス(9,9-ジメチルフルオレン-2-イル)-[1,1-ビフェニル]-4,4'-ジアミン(FFD)等の基を有するビニルモノマーが好ましく使用できる。

【0013】本発明に使用する不飽和基を有するアクリル酸エステル又はメタクリル酸エステルモノマーについて、その不飽和基は、炭素数が2から20の不飽和炭化水素残基が好ましく、例えばビニル、アリル、シクロペンタジエニル基などが適用可能である。不飽和炭化水素残基を有するアクリル系不飽和ビニルモノマーの具体例としてはビニルアクリレート、ビニルメタクリレート、アリルアクリレート、アリルメタクリレート、クロチルアクリレート、クロチルメタクリレート、シクロペンタジエニルアクリレート、シクロペンタジエニルメタクリレート等が挙げられる。

【0014】本発明の高分子正孔輸送材は上述したように特定の置換基を有するビニルモノマーと特定の不飽和基を有するアクリル酸エステル又はメタクリル酸エステルとの共重合体であるが、前記置換基を有するビニルモノマーの構成モノマー全体に対する構成比率は0.5乃至0.9の範囲であることが好ましく、0.6乃至0.9の範囲がさらに好ましい。また、前記共重合体の重合度は10乃至100000の範囲であることが好ましく、1000乃至50000の範囲がより好ましい。

【0015】本発明の請求項1の発明に係る特定置換基を有するビニルモノマーと特定不飽和基を有するアクリル酸エステル又はメタクリル酸エステルとの共重合体は、その製法は限定するものではないが、通常、共重合

はラジカル重合により達成される。重合開始剤としては通常公知のラジカル重合開始剤が使用できる。たとえば、パーオキシド化合物、アゾ化合物、レドックス化合物等が挙げられる。具体的にはパーオキシド化合物としては、クメンパーオキシド、*m*-ブチルパーオキシド、ジクミルパーオキシド、過酸化ベンゾイルなどが挙げられる。アゾ化合物としてはアゾビスイソブチロニトリル等が挙げられる。レドックス化合物としてはギ酸と2価鉄イオンの組み合わせ、過酸化ベンゾイルとジメチルアニリンの組み合わせ、塩化ベンジルとN,N-ジメチルアニリンの組み合わせ等の開始剤が用いられるがこれらの例示化合物に限定されるものではない。

【0016】共重合時に使用される溶媒は特に限定されず、使用するモノマーと開始剤の選択により選定される。たとえば、乳化重合の場合は溶媒は水で、少量の界面活性剤が使用される。溶液重合の場合に使用される溶媒としてはメタノール、エタノール、プロパノール、ブタノール、オクタノールなどのアルコール類、アセトン、メチルエチルケトンなどのケトン類、ジエチルエーテル、ジブチルエーテル、テトラヒドロフラン、ジオキサン、クラウンエーテルなどのエーテル類、酢酸、プロピオン酸、酪酸、2-エチルヘキサン酸などのカルボン酸類、酢酸エチル、酢酸ブチル、2-エチルヘキサン酸エチルなどのエステル類、トリエチルアミン、トリプロピルアミン、トリブチルアミン、ジエチルアミン、ジプロピルアミン、ジブチルアミンなどのアミン類、ホルムアミド、N,N-ジメチルホルムアミド、N,N-ジメチルアセトアミドなどのアミド類、ヘキサン、ヘプタン、オクタン、シクロヘキサンなどの脂肪族炭化水素、ベンゼン、トルエン、キシレンなどの芳香族炭化水素、クロロホルム、ジクロロメタン、1,2-ジクロロエタン、クロルベンゼン、ジクロロベンゼンなどのハロゲン化炭化水素などが挙げられる。

【0017】重合温度は-20℃から使用する溶媒の沸点まで可能であり特に限定されないが、好ましくは0～50℃の範囲の温度である。重合圧力も特に限定されるものではなく常圧から100kg/cm²で行われる。重合時間は使用するモノマーの重合速度により異なるが通常10分から50時間の範囲で行われる。

【0018】前記共重合体の構成モノマーとして、置換基を有するビニルモノマーとしてビニルカルバゾールを用いて有機電界発光素子を作製する場合、得られる共重合体は、正孔輸送材料および発光層材料として使用することができる。発光層材料として用いられるときには公知の有機蛍光材料を添加される。有機蛍光材料の代表例としては、緑色蛍光材料としてクマリン-6、キナクリドンなど、青色蛍光材料としてはペリレン、ルブレンなど、赤色蛍光材料としてはユウロピウムのジケトン錯体が用いられるがこれらの化合物に限定されるものではない。これらの有機蛍光材料の使用量は化合物によって異

なるが、本発明により得られる共重合体に対し、0.01～5%程度である。この範囲より少なくなると発光効率が低く、多くなると濃度消光により発光効率は低下する。好ましくは0.05～3%の範囲である。

【0019】本発明の共重合体をホスト材とし、これに三重項発光材料をドーピングすることができる。三重項発光材料としては、たとえばイリジウム錯体、白金錯体が用いられる。配位子にフェニルピリジン、チオフェニルピリジンおよびその誘導体を配位子としたイリジウム錯体または白金錯体またはポルフィリンの白金錯体などが用いられるが、特にこれらの化合物に限定されるものではない。これらの三重項発光材料の使用量は化合物によって異なるが、本発明により得られる共重合体に対し、0.1～10%程度である。この範囲より少なくなると発光効率が低く、多くなると濃度消光により発光効率は低下する。好ましくは0.5～5%の範囲である。

【0020】本発明の共重合体は溶媒溶解性が高く種々の溶媒に溶解し、その溶液からスピンコート法、バーコート法、ディップコート法、フローコート法、スクリーン印刷法、インクジェットプリンティング法などの簡便な塗布方式で容易に薄膜を作製することができる。溶媒としては前記重合溶媒と同じ有機溶媒が使用できる。本発明の高分子の溶媒に対する溶解度は高分子の種類、分子量によって異なるため使用する高分子に最良の溶媒を選択する必要がある。さらに上記の方法による薄膜作製時には共重合体を溶解した溶液の粘度が重要な因子となるため、薄膜方法とそのプロセスをも考慮して溶媒を選択する必要がある。

【0021】本発明に使用する溶媒の好ましい例を具体的に挙げるならば、アセトン、メチルエチルケトンなどのケトン類、ジブチルエーテル、テトラヒドロフラン、などのエーテル類、酢酸エチル、酢酸ブチル、2-エチルヘキサン酸エチルなどのエステル類、ホルムアミド、N,N-ジメチルホルムアミド、N,N-ジメチルアセトアミドなどのアミド類、ヘキサン、ヘプタン、オクタン、シクロヘキサンなどの脂肪族炭化水素、ベンゼン、トルエン、キシレンなどの芳香族炭化水素、クロロホルム、ジクロロメタン、1,2-ジクロロエタンなどのハロゲン化炭化水素、N,N-ジメチルアセトアミド、N,N-ジメチルホルムアミドに代表されるアミド化合物、メトキシエタノール、フェノキシエタノールなどのアルコール類などがある。これらの溶媒を混合して使用することも可能である。これらの最適溶媒を選択し溶解した後、上記方法で薄膜を作製し、室温または加熱下に常圧または減圧下で乾燥して任意の膜厚の薄膜を作製することができる。

【0022】本発明の共重合体の薄膜を作製し、その上にさらに薄膜の積層を試みる場合、通常の方法だと先に作製した薄膜が、後から製膜しようとするポリマー溶液の溶媒に溶解し、きれいな多層の積層薄膜ができない。

【0023】この問題を解決するため、本発明の共重合

体又は溶液に光重合開始剤を加え、製膜した薄膜に光照射することにより硬化して溶媒に不溶化することができる。この方法により高品質の多層薄膜の積層化を達成できる。ここで、光照射とは主として紫外線照射を意味するが紫外線に限るものではなく可視光も含んでいる。

【0024】また、所定の開口パターンを有するフォトマスクを作製した薄膜の上方に覆い光照射することにより選択的に溶媒不溶化された部分と、光照射されなかった溶媒不溶化されない部分が形成され、該溶媒不溶化されない部分を溶剤によりエッチング除去された結果、該

マスクの開口パターン形状が形成できる。
【0025】本発明において使用できる光重合開始剤としては、カルボニル化合物としてベンゾフェノン、チオキサントン等の芳香族ケトン類、アセトフェノン、2-ヒドロキシ-2-メチルプロピオフェノン、2,2-ジメトキシ-2-フェニルアセトフェノン、ベンゾインエーテル等のアセトフェノン類、ベンジル、メチルベンゾイルホルメート等のジケトン類、2,4,6-トリメチルベンゾイルホスフィンオキシド等のアシルホスフィンオキシド類、テトラメチルチウラムジスルフィド等の硫黄化合物、過酸化ベンゾイル等の有機過氧化物、アゾビスイソブチロニトリル等のアゾ化合物が挙げられる。

【0026】光重合開始剤を使用する際、光重合開始剤は光を吸収してラジカルを発生するので、光源からの吸収領域によく適合すること、硬化速度が大きいこと、ポリマー溶液との相溶性がよいこと、安価なことなどを考慮して選択する必要がある。光重合開始剤の使用量は前記共重合体に対し0.5~20%程度、好ましくは1~10%である。

【0027】硬化速度を速め、基板との付着力を高めるため、架橋助剤を使用することができる。架橋助剤としては不飽和炭化水素残基、アジド基、アゾ基、ニトリル基、ケイ皮酸基などを有する多官能モノマーなどが用いられる。具体的には、二官能スチレン誘導体、二官能ビニルエーテル、芳香族ジビニル化合物、芳香族ビスアジド、ジアゾナフトキノンなどが挙げられる。好ましくは、ジビニルベンゼン、フタル酸ジアリル、3,3'-ジアジドフェニルスルフォラン、4,4'-ジアジド-2,2'-ジメトキシビフェニル等である。

【0028】次に、本発明の有機電界発光素子の構造について述べる。本発明の有機電界発光素子は、陽極と陰極との間に発光層を含む1層または複数層の有機薄膜層を積層した構造である。例えば、基板/陽極/発光層/陰極が順に積層された構造、基板/陽極/正孔輸送層/発光層/陰極が順に積層された構造、基板/陽極/緩衝層/発光層/陰極が順に積層された構造、基板/陽極/正孔輸送層/緩衝層/発光層/陰極が順に積層された構造などが挙げられる。

【0029】陽極は正孔輸送層、発光層などに正孔を供給するものであり、ガラスなどの基板上に形成される。

本発明に用いられる陽極材料は特に限定されず、具体例としては酸化インジウム錫(ITO)、酸化錫などの導電性金属酸化物や金、銀、白金などの金属が挙げられる。また、市販のITO付ガラスを使用することもできる。市販のITO付きガラスは通常、洗剤、溶剤で洗浄、またはUVオゾン照射装置またはプラズマ照射装置により洗浄され、使用される。

【0030】陰極は発光層に電子を供給するものであり、本発明に用いられる陰極材料としては特に限定されず、一般に使用されているものであれば何を使用してもよい。具体例としては、Mg、Ag、Ca、Al等の金属やそれらの合金、たとえばMg-Ag合金、Mg-Al合金などが挙げられる。

【0031】

【実施例】次に、本発明を実施例によって更に具体的に説明するが、本発明は以下の実施例の記載に限定されるものではない。

【0032】[合成例1] N-ビニルカルバゾールとメタクリル酸ビニルの共重合体の合成

300mlのフラスコにN-ビニルカルバゾールの12g(63mmol)とメタクリル酸ビニル2.7g(24mmol)アゾビスイソブチロニトリル0.5gを加え、トルエン240mlを加えて溶解した。密栓した後、60℃の雰囲気下に48時間静置し共重合した。1000mlのメタノール中に注ぎ過し、メタノールで洗浄後、50℃で真空乾燥して14.4g(収率98%)の白色粉末を得た。分析の結果、N-ビニルカルバゾールのビニル基とメタクリル酸ビニルのメタクリル基が重合し、メタクリル酸ビニルのビニル基が側鎖として存在する共重合体であることがわかった。分子量は15,000であった。

【0033】[合成例2] 9-n-デシル-3-エチニルカルバゾールの重合

回転子を入れた100mlのフラスコに9-n-デシル-3-エチニルカルバゾールの1g(3.15mmol)を加えて充分窒素置換し、窒素雰囲気下に溶媒として50mlのジメチルホルムアミドと触媒として[Rh(ノルボルナジエン)Cl]₂の10mg(0.022mmol)および助触媒としてトリエチルアミン222mg(2.2mmol)を加え、30℃で2時間攪拌し重合した。重合終了後、500mlのメタノール中に注ぎ、粉末状ポリマーを得た。過し、メタノールで洗浄後、50℃で3時間真空乾燥した。0.9gのオレンジ色のポリマーを得た。重合収率は90%であった。

【0034】[合成例3] 高分子金属錯体(PAA·Sal)Alq₂の合成

回転子を入れた1000mlのフラスコにサリチルアルデヒド21gを精秤し、メタノール500mlを加えた。これに、ポリアリルアミン(日東紡製、PAA-10C、分子量約1万、10wt%水溶液)100mlを

ゆっくりと添加したところ、添加開始と同時に黄色の結晶が生成した。添加終了後約1時間攪拌し、析出した結晶を濾過、メタノールで洗浄、乾燥して28gの黄色結晶を得た。以後、得られた高分子重合体をPAA・Sa1と略す。次に、500mlのフラスコに上記で製造したPAA・Sa1(2.8g, 17.5mmol)をN,N-ジメチルアセトアミドの100mlに溶解し、この溶液にAl(NO₃)₃・9H₂O(6.5g, 17.5mmol)を加え、更に8-キノリノール(5.0g, 35mmol)をN,N-ジメチルアセトアミド50mlに溶解して加えた。すると均一で澄明な淡黄色の溶液が得られた。この系に25%のアンモニア水をゆっくりと加えると、淡黄色の均一溶液が生成した。pH9までアンモニア水を加えて、1時間攪拌した後、1000mlの蒸留水中に注ぐと黄色の粉末が生成した。生成した沈殿を濾過し、水洗後、乾燥して8.1gの高分子金属錯体を得た。

【0035】[実施例1]有機電界発光素子を次のように作製した。合成例1で合成したN-ビニルカルバゾールとメタクリル酸ビニルの共重合体の200mgをトルエン5mlに溶解し、光重合開始剤として2,2-ジメトキシ-2-フェニルアセトフェノンを10mg加えて溶解した。洗浄処理した市販のITO付ガラス(15Ω/□以下;セントラル硝子製)の上にスピニングして薄膜を作製し減圧下に乾燥した。フォトマスクをつけて、254~365nmに主波長を有する紫外線を照射し得られた薄膜をフォトマスクの所定のパターン状に硬化し、溶媒不溶化した。次に部分硬化した薄膜をトルエン溶媒中に浸漬してエッチングし、膜厚50nmのマスクパターン状の正孔輸送材層を得た。次に、合成例4で試作した高分子金属錯体(PAA・Sal)Alq2の100mg(0.21mmol)をクロロホルム5mlに溶解した。この溶液を正孔輸送層の上にスピニング法により塗布して乾燥し、膜厚110nmの薄膜を作製した。次に、真空状着装置を用いて陰極としてMg:Ag=20:1を共蒸着により200nmの膜厚で製膜した。こうして作製した発光素子を減圧できる測定治具中にセットし、減圧しながら直流電圧を印可し発光輝度を測定したところ、駆動電圧12Vで1300cd/m²の輝度を得た。

【0036】〔実施例2〕有機電界発光素子を次のように作製した。合成例1で合成したビニルカルバゾールと

メタクリル酸ビニルの共重合体の200 mgをトルエン5 mlに溶解し、光重合開始剤として2, 2-ジメトキシ-2-フェニルアセトフェノンを10 mg加えて溶解し、洗浄した市販のITO付ガラス(15 Ω /□以下: セントラル硝子製)の上にスピンコートして薄膜を作製し減圧下に乾燥した。フォトマスクをつけて、254~365 nmに主波長を有する紫外線を照射し薄膜を硬化し得られた薄膜をフォトマスクの所定のパターン状に硬化し、溶媒不溶化した。次に部分硬化した薄膜をトルエン溶媒中に浸漬してエッチングし、膜厚50 nmのマスクパターン状の正孔輸送材層を得た。次に、合成例2で示した9-n-デシル-3-エチニルカルバゾール重合体100 mg(0.32 mmol)をテトラヒドロフラン5 mlに溶解し、この溶液にトリス(2-フェニルピリジン)イリジウム錯体8 mg(0.1 mmol)を加えて溶解し、溶液を正孔輸送層の上にスピンコート法により膜厚25 nmの薄膜を作製した。次に、真空状着装置を用いて、バソクプロインを膜厚10 nm、Alq3を膜厚23 nm、および陰極としてMg:Ag=20:1を共蒸着により200 nmの膜厚で製膜した。こうして作製した発光素子を減圧できる測定治具中にセットし、減圧しながら直流電圧を印加し発光輝度を測定したところ、12 vで5500 cd/m²の輝度を得た。

【0037】

【発明の効果】以上説明したように、有機電界発光素子を製造するときに、本発明の共重合体を使用して下地の薄膜を作製し、光照射により硬化、溶媒不溶化することにより、上から塗布される有機薄膜層の溶媒による下地の溶解の問題が皆無となった。従って、同じ方法を繰り返して適用することにより、有機薄膜の積層を容易に行うことができる。また、この事実是有機薄膜をスピンコート法、バーコート法、ディップコート法、フローコート法、スクリーン印刷法、インクジェットプリンティング法などの経済性の高くしかも簡便な塗布方式で多層製膜するための技術の確立を意味する。さらに、このような塗布方式による製膜方法は、真空蒸着法に対し、大面積化、生産コストの低下、加工性などの点で非常に有利である。さらに、本方法で高効率の有機電界発光素子が作製できることは産業上有用な発明である。さらにまた、

40 本発明は有機電界発光素子のみならず、有機薄膜を多層に積層するような用途全てに適用できることはいうまでもない。

JAPANESE

[JP,2003-142272,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE
INVENTION TECHNICAL PROBLEM MEANS EXAMPLE

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates two or more organic thin films to the organic electroluminescence devices which used the macromolecule electron hole transport material and it in which a laminating is possible.

[0002]

[Description of the Prior Art] There are inorganic electroluminescence devices which consist of an inorganic material, and organic electroluminescence devices which consist of an organic material as electroluminescence devices. Since it says that luminescence of high brightness is obtained by the low battery in recent years, organic electroluminescence devices attract attention.

[0003] Generally, organic electroluminescence devices form organic thin film layers, such as an electron hole transporting bed and a luminous layer, on the glass plate which vapor-deposited the thin film of anode materials, such as an indium stannic-acid ghost (ITO), form the thin film of a cathode material on it further, and are made. The ingredient used for organic thin film stratification, such as an electron hole transporting bed and a luminous layer, is divided roughly into a low-molecular ingredient and polymeric materials. The difference between a low-molecular ingredient and polymeric materials is based on the film production approach. For example, when the low-molecular ingredient represented by aluminum tris quinolinol (it omits the following Alq3) is used, vacuum deposition is required to produce a thin film, and working efficiency is bad. In that respect, when polymeric materials are used, a film can be produced from the solution by simple spreading methods, such as a spin coat method, the bar coat method, a dip coating method, the flow coat method, screen printing, and the ink jet printing method. Furthermore, the film production approach by such spreading method is dramatically advantageous in respect of large-area-izing, lowering of a production cost, workability, etc. to a vacuum deposition method.

[0004] Various polymeric materials are developed as the electron hole transport material for organic electroluminescence devices, and luminescence material. For example, the ingredient (Kogino, H.Sato, et al, Macromol.Rapid commun.20,103-106 (1999)) macromolecule-ized with the derivative of a triphenylamine as electron hole transport material is known. As macromolecule luminescence material, the polymer (M. Inbasekaran, E.Woo, et al, Synth.metals, 111-112,397 (2000), I.S.Millard, ibid.111-112,119 (2000)) of the poly fluorene system etc. is known. Moreover, the polyvinyl carbazole is studied by both electron hole transport material and luminescence material (J. Kido, et al, Appl.Phys.Lett. 63, 2627, (1993)). If use the electron hole transport material of these macromolecule systems, and luminescence material as a solution, a film is produced by the above-mentioned approaches, such as a spin coat, the following layer is produced by the still more nearly same approach and a laminating is tried, the thin film which produced the film previously will dissolve in the solvent of the polymer solution which is going to produce a film later, and a beautiful multilayer laminating thin film will not be made.

[0005] The polymer with long conjugated system like polyphenylene vinylene (Following PPV and

abbreviation) is known well. However, since PPV is insoluble to a solvent also in polymeric materials, it cannot apply as it is. When insoluble [to a solvent] also in such polymeric materials, a precursor is compounded, and after making it a thin film with a spin coat method etc., it must change into the specified substance by heat-treatment, and a routing becomes complicated.

[0006]

[Problem(s) to be Solved by the Invention] As mentioned above, the satisfactory thing is not obtained although research of the polymeric materials for organic electroluminescence devices with easy thin-film-izing is made briskly.

[0007] A thin film is hardened and insolubilized by irradiating light, such as the light and ultraviolet rays, at the electron hole transport ingredient thin film which has the partial saturation radical of a macromolecule, and if the ingredient which carries out the laminating of the thin film of this ingredient or a dissimilar material at a it top is obtained, manufacture of organic electroluminescence devices will become very easy, and moreover, a large area component will be made easily and becomes a very effective means on industry. Therefore, it accomplishes as a technical problem that invention solves the problem mentioned above.

[0008]

[Means for Solving the Problem] The giant-molecule electron hole transport material of this invention consists of a copolymer of the vinyl monomer which has a substituent so that it may indicate to (1) claim 1, and the acrylic ester or methacrylic ester which has a partial saturation radical, and it is characterized by this substituent being at least one sort chosen from the group of a carbazole radical, a carbazole derivative radical, a triphenylamine radical, and a triphenylamine derivative radical.

(2) As for a partial saturation radical, in (1), it is desirable that it is the aliphatic-unsaturated-hydrocarbon residue whose carbon numbers are 2 thru/or 20 so that it may indicate to claim 2.

(3) As for the percentage to the whole configuration monomer of the vinyl monomer which has said substituent, in the copolymer in (1) thru/or (2), it is desirable that it is the range of 0.5 thru/or 0.9 so that it may indicate to claim 3.

(4) As for the polymerization degree of the copolymer in (1) thru/or (3), it is desirable that it is the range of 10 thru/or 100000 so that it may indicate to claim 4.

[0009] Moreover, the organic thin film which is an organic electrolytic luminescence component possessing the layer which consists of an organic thin film of one or more layers which has a luminous layer at least, and touches between an anode plate and cathode at this luminous layer or this luminous layer is characterized by including the macromolecule electron hole transport material of a publication in (1) thru/or (4) so that the organic electrolytic luminescence component of this invention may be indicated to (5) claim 5.

(6) In the organic electroluminescence devices possessing the electron hole transporting bed and luminous layer which consist of an organic thin film between an anode plate and cathode, that solvent insolubilization was carried out [that] by the photoreaction in the thin film with which this electron hole transporting bed is set to (1) thru/or (4) from the macromolecule electron hole transport material of a publication is preferably applied so that it may indicate to claim 6.

(7) As a result of being carried out the etching clearance of the electron hole transporting bed in (6) with a solvent in the part in which solvent insolubilization was selectively carried out by the bonnet light exposure with the mask which has a predetermined opening pattern, and the part by which this solvent insolubilization of the part by which an optical exposure was not carried out, and by which solvent insolubilization is not carried out is not formed and carried out, the thing in which it comes to be formed the opening pattern configuration of this mask is preferably applied, so that it may indicate to claim 7.

[0010] Thus, the organic electroluminescence devices built over this invention by constituting can be produced by simple spreading methods, such as a spin coat method, a dip coating method, and the ink jet printing method, without using vacuum evaporation technique at the time of film production of the ingredient.

[0011]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail. The substituent needs to

have electron hole transport ability, and the vinyl monomer which has the substituent used for this invention can use at least one sort chosen from the group of a carbazole radical, a carbazole derivative radical, a triphenylamine radical, and a triphenylamine derivative radical as such a substituent.

[0012] More specifically, the vinyl monomer which has a carbazole radical and an alkylation carbazole radical can use it preferably as a carbazole system. As a triphenylamine system, a triphenylamine, N, N'-screw (3-methylphenyl)-N, N'-diphenyl [1 and 1'-biphenyl]-4, 4'-diamine (TPD), 4, 4', and 4'' - tris [1-naphthyl (phenyl) amino] triphenylamine (1-TNATA) -- 4, 4', and 4'' - tris [2-naphthyl (phenyl) amino] triphenylamine (2-TNATA) -- 4, 4', and 4'' - tris [biphenyl-4-IRU-(3-methylphenyl) amino] triphenylamine (p-PMTDATA) -- 4, 4', and 4'' - tris [9 and 9-dimethyl fluorene-2-IRU (phenyl) amino] triphenylamine (TFATA) -- 4, 4', and 4'' - tris (N-carbazoyl) triphenylamine (TCTA), 1, 3, 5-tris-[N-(4-diphenyl aminophenyl) phenylamino] benzene (p-DPA-TDAB), 1, 3, 5-tris {4-[methylphenyl (phenyl) amino] phenyl} benzene (MTDAPB), N, N'-JI (biphenyl-4-IRU)-N, N'-diphenyl [1 and 1'-biphenyl]-4, 4'-diamine (p-BPD), N, N'-screw (9 and 9-dimethyl fluorene-2-IRU)-N, the N'-diphenyl fluorene -2, and 7-diamine (PFFA), N, N, N', and the vinyl monomer that has radicals, such as N'-tetrakis (9 and 9-dimethyl fluorene-2-IRU)-[1 and 1-biphenyl]-4 and 4'-diamine (FFD), can use it preferably.

[0013] About the acrylic ester or the methacrylic ester monomer which has the partial saturation radical used for this invention, the unsaturated hydrocarbon residue of 2 to 20 has a desirable carbon number, for example, the partial saturation radical can apply vinyl, an allyl compound, a cyclopentadienyl group, etc. As an example of the acrylic partial saturation vinyl monomer which has unsaturated hydrocarbon residue, vinyl acrylate, vinyl methacrylate, allyl compound acrylate, allyl compound methacrylate, clo chill acrylate, clo chill methacrylate, cyclopentadienyl acrylate, cyclopentadienyl methacrylate, etc. are mentioned.

[0014] Although the giant-molecule electron hole transport material of this invention is a copolymer with the acrylic ester or methacrylic ester which has the vinyl monomer which has a specific substituent, and a specific partial saturation radical as mentioned above, as for the percentage to the whole configuration monomer of the vinyl monomer which has said substituent, it is desirable that it is the range of 0.5 thru/or 0.9, and its range of 0.6 thru/or 0.9 is still more desirable. Moreover, as for the polymerization degree of said copolymer, it is desirable that it is the range of 10 thru/or 100000, and it is more desirable. [of the range of 1000 thru/or 50000]

[0015] Although the copolymer with the acrylic ester or methacrylic ester which has the vinyl monomer which has a specific substituent concerning invention of claim 1 of this invention, and a specific partial saturation radical does not limit the process, copolymerization is usually attained by the radical polymerization. As a polymerization initiator, a well-known radical polymerization initiator can usually be used. For example, a peroxide compound, an azo compound, a redox compound, etc. are mentioned. Specifically as a peroxide compound, cumene peroxide, t-butyl peroxide, JIKUMIRU peroxide, a benzoyl peroxide, etc. are mentioned. Azobisisobutyronitril etc. is mentioned as an azo compound. Although initiators, such as combination of a formic acid and divalent iron ion, combination of a benzoyl peroxide and dimethylaniline, and combination of a benzyl chloride and N,N-dimethylaniline, are used as a redox compound, it is not limited to these instantiation compounds.

[0016] Especially the solvent used at the time of copolymerization is not limited, but is selected by selection of the monomer and initiator to be used. For example, in the case of an emulsion polymerization, a solvent is water and the surfactant of a small amount is used. As a solvent which is used in the case of solution polymerization, a methanol, ethanol, Alcohols, such as propanol, a butanol, and an octanol, an acetone, Ketones, such as a methyl ethyl ketone, diethylether, dibutyl ether, Ether, such as a TECHIRA hydronalium furan, dioxane, and crown ether, Carboxylic acids, such as an acetic acid, a propionic acid, butanoic acid, and 2-EKIRU hexanoic acid Ester, such as ethyl acetate, butyl acetate, and 2-ethylhexanoic acid ethyl Triethylamine, tripropylamine, tributylamine, diethylamine, Amines, such as a dipropyl amine and dibutyl amine, a formamide, Amides, such as N,N-dimethylformamide and N,N-dimethylacetamide Aliphatic hydrocarbon, such as a hexane, a heptane, an octane, and a cyclohexane, Halogenated hydrocarbon, such as aromatic hydrocarbon, such as benzene, toluene, and a xylene, chloroform, dichloromethane, 1, 2-JIKUROKU ethane, chlorobenzene, and

dichlorobenzene, etc. is mentioned.

[0017] Although polymerization temperature is especially possible till the boiling point of the solvent used from -20 degrees C and it is not limited, it is the temperature of the range of 0-50 degrees C preferably. Especially the polymerization pressure force is not limited, either and it is carried out by 100kg/cm² from ordinary pressure. Although polymerization time amount changes with rate of polymerizations of the monomer to be used, it is usually performed in 50 hours from 10 minutes.

[0018] When producing organic electroluminescence devices as a configuration monomer of said copolymer, using vinylcarbazole as a vinyl monomer which has a substituent, the copolymer obtained can be used as an electron hole transport ingredient and a luminous layer ingredient. When used as a luminous layer ingredient, a well-known organic fluorescence ingredient is added. As an example of representation of an organic fluorescence ingredient, although the diketone complex of a europium is used as red fluorescence ingredients, such as perylene and rubrene, as blue fluorescence ingredients, such as a coumarin -6 and Quinacridone, as a green fluorescence ingredient, it is not limited to these compounds. Although the amount of these organic fluorescence ingredients used changes with compounds, it is about 0.01 - 5% to the copolymer obtained by this invention. If luminous efficiency is low when it becomes less than this range, and it increases, luminous efficiency will fall by concentration quenching. It is 0.05 - 3% of range preferably.

[0019] The copolymer of this invention is made into host material, and it is **. Triplet luminescent material can be doped to this. As a triplet luminescent material, an iridium complex and a platinum complex are used, for example. Although the iridium complex which made the ligand a phenyl pyridine, a thiophenyl pyridine, and its derivative, a platinum complex, or the platinum complex of a porphyrin is used for a ligand, it is not limited to especially these compounds. Although the amount of such triplet luminescent material used changes with compounds, it is about 0.1 - 10% to the copolymer obtained by this invention. If luminous efficiency is low when it becomes less than this range, and it increases, luminous efficiency will fall by concentration quenching. It is 0.5 - 5% of range preferably.

[0020] Solvent solubility can dissolve the copolymer of this invention in various high solvents, and a thin film can be easily produced from the solution by simple spreading methods, such as a spin coat method, the bar coat method, a dip coating method, the flow coat method, screen printing, and the ink jet printing method. The organic solvent same as a solvent as said polymerization solvent can be used. The solubility to the solvent of the macromolecule of this invention needs to choose the best solvent as the macromolecule used since it changes with the class of macromolecule, and molecular weight. Since the viscosity of the solution which dissolved the copolymer serves as an important factor at the time of thin film production by the further above-mentioned approach, it is necessary to choose a solvent also in consideration of the thin film approach and its process.

[0021] If the desirable example of the solvent used for this invention is given concretely, an acetone, Ketones, such as a methyl ethyl ketone, dibutyl ether, a TECHIRA hydronalium furan, Ester, such as which ether, ethyl acetate, butyl acetate, and 2-ethylhexanoic acid ethyl Amides, such as a formamide, N,N-dimethylformamide, and N,N-dimethylacetamide Aliphatic hydrocarbon, such as a hexane, a heptane, an octane, and a cyclohexane, Aromatic hydrocarbon, such as benzene, toluene, and a xylene, chloroform, There are alcohols, such as an amide compound represented by halogenated hydrocarbon, such as dichloromethane and 1,2-dichloroethane, N,N-dimethylacetamide, and N,N-dimethylformamide, methoxy ethanol, and phenoxyethanol, etc. It is also possible to mix and use these solvents. After choosing these optimal solvents and dissolving, ** which produces a thin film by the above-mentioned approach, dries under ordinary pressure or reduced pressure, and produces the thin film of the thickness of arbitration under a room temperature or heating is made.

[0022] When producing the thin film of the copolymer of this invention and trying the laminating of a thin film further on it, the thin film previously produced when it was the usual approach dissolves in the solvent of the polymer solution which is going to produce a film later, and a beautiful multilayer laminating thin film is not made.

[0023] Since this problem is solved, it can harden by carrying out an optical exposure to the thin film which added the photopolymerization initiator to the copolymer or solution of this invention, and

produced the film, and can insolubilize to a solvent. Lamination of the multilayered film of high quality can be attained by this approach. Here, although an optical exposure mainly means UV irradiation, it does not restrict to ultraviolet rays and the light is also included.

[0024] Moreover, as a result of forming the part by which solvent insolubilization was selectively carried out by carrying out a bonnet light exposure, and the part by which an optical exposure was not carried out and by which solvent insolubilization is not carried out above the thin film which produced the photo mask which has a predetermined opening pattern and carrying out etching clearance of this part by which solvent insolubilization is not carried out with a solvent, the opening pattern configuration of this mask can be formed.

[0025] As a photopolymerization initiator which can be used in this invention As a carbonyl compound, aromatic ketone, such as a benzophenone and a thioxan ton An acetophenone, 2-hydroxy-2-methyl-propiophenone, Acetophenones, such as a 2 and 2-dimethoxy-2-phenyl acetophenone and the benzoin ether Acyl phosphine oxide, such as diketones, such as benzyl and methyl benzoyl formate, 2 and 4, and 6-trimethyl benzoyl phosphine oxide Azo compounds, such as organic peroxide, such as sulfur compounds, such as tetramethylthiuramdisulfide, and a benzoyl peroxide, and azobisisobutyronitril, are mentioned.

[0026] It is suiting an absorption field well from the light source, since a photopolymerization initiator absorbs light in case a photopolymerization initiator is used, and a radical is generated, and that a cure rate is large. Compatibility with a polymer solution needs to choose in consideration of a good thing, a cheap thing, etc. The amount of the photopolymerization initiator used is 1 - 10% preferably about 0.5 to 20% to said copolymer.

[0027] In order to speed up a cure rate and to heighten adhesion force with a substrate. A bridge formation assistant can be used. The polyfunctional monomer which has unsaturated hydrocarbon residue, an azide radical, azo, a nitrile group, a cinnamic-acid radical, etc. as a bridge formation assistant is used. Specifically, a 2 organic-functions styrene derivative, 2 organic-functions vinyl ether, an aromatic series divinyl compound, aromatic series bis-diazido, a diazo naphthoquinone, etc. are mentioned. Preferably, they are a divinylbenzene, diallyl phthalate, 3, 3'-diazido phenyl sulfolane, 4, 4'-diazido -2, a 2'-dimethoxy biphenyl, etc.

[0028] Next, the structure of the organic electroluminescence devices of this invention is described. The organic electroluminescence devices of this invention are the structure which carried out the laminating of the organic thin film layer (one layer or two or more layers) containing a luminous layer between an anode plate and cathode. For example, the structure where the laminating of a substrate / anode plate / luminous layer / the cathode was carried out to order, the structure where the laminating of a substrate / anode plate / electron hole transporting bed / luminous layer / the cathode was carried out to order, the structure where the laminating of a substrate / anode plate / buffer coat / luminous layer / the cathode was carried out to order, the structure where the laminating of a substrate / anode plate / electron hole transporting bed / buffer coat / luminous layer / the cathode was carried out to order, etc. are mentioned.

[0029] An anode plate supplies an electron hole to an electron hole transporting bed, a luminous layer, etc., and is formed on substrates, such as glass. Especially the anode material used for this invention is not limited, but metals, such as conductive-metallic-oxide metallurgy, such as indium oxide tin (ITO) and tin oxide, silver, and platinum, are mentioned as an example. Moreover, commercial glass with ITO can also be used. With a detergent and a solvent, the commercial glass with ITO is washed by washing, UV ozone irradiation equipment, or plasma irradiation equipment, and is usually used.

[0030] Cathode supplies an electron to a luminous layer, is not limited especially as a cathode material used for this invention, but as long as it is generally used, it may use anything. As an example, metals and those alloys, for example, a Mg-Ag alloy, such as Mg, Ag, calcium, and aluminum, a Mg-aluminum alloy, etc. are mentioned.

[0031]

[Example] Next, although an example explains this invention still more concretely, this invention is not limited to the publication of the following examples.

[0032] 12g (63mmol) of N-vinylcarbazole and methacrylic-acid vinyl 2.7g (24mmol)

azobisisobutyronitril 0.5g were added to the flask of 300ml of composition of the copolymer of [synthetic example 1] N-vinylcarbazole and methacrylic-acid vinyl, toluene 240ml was added, and it dissolved. After sealing, it put gently on the bottom of a 60-degree C ambient atmosphere for 48 hours, and copolymerized. It poured and filtered in the 1000ml methanol, the vacuum drying was carried out at 50 degrees C after washing with the methanol, and 14.4g (98% of ****) white powder was obtained. The vinyl group of N-vinylcarbazole and the methacrylic radical of methacrylic-acid vinyl carried out the polymerization, and analysis showed that it was the copolymer with which the vinyl group of methacrylic-acid vinyl exists as a side chain. Molecular weight was 15,000.

[0033] Add 1g (3.15mmol) of a 9-n-DESHIRU-3-ethynyl carbazole to the 100ml flask into which the polymerization rotator of a [synthetic example 2] 9-n-DESHIRU-3-ethynyl carbazole was put, and a nitrogen purge is enough carried out to it. Triethylamine 222mg (2.2mmol) was added as 10mg (0.022mmol) and the co-catalyst of 2 as 50ml dimethylformamide and a catalyst as a solvent to the bottom of nitrogen-gas-atmosphere mind, at 30 degrees C, it agitated for 2 hours and the polymerization was carried out (norbornadiene). It poured after polymerization termination and into the 500ml methanol, and the powdered polymer was obtained. It filtered and the vacuum drying was carried out at 50 degrees C after washing with the methanol for 3 hours. The polymer of 0.9g orange was obtained. Polymerization **** was 90%.

[0034] Salichlaldehyde 21g was weighed precisely in the 1000ml flask into which the synthetic rotator of the [synthetic example 3] polymer metal complex (PAA-Sal) Alq2 was put, and methanol 500ml was added. When poly allylamine (Nittobo make, PAA-10C, molecular weight 10,000 [about], 10wt% water solution) 100ml was slowly added to this, the yellow crystal generated to addition initiation and coincidence. After addition termination, it agitated for about 1 hour, and the methanol washed [filtration and] the depositing crystal, it dried, and the 28g yellow crystal was obtained. Henceforth, the obtained macromolecule polymer is abbreviated to PAA-Sal. Next, PAA-Sal (2.8g, 17.5mmol) manufactured above was dissolved in the 500ml flask at 100ml of N,N-dimethylacetamide, aluminum(NO3)3.9H2O (6.5g, 17.5mmol) was added to this solution, and the eight quinolinol (5.0g, 35mmol) was further dissolved and added to 50ml of N,N-dimethylacetamide. Then, the solution of uniform and clear light yellow was obtained. When 25% of aqueous ammonia was slowly added to this system, the homogeneity solution of light yellow generated. After adding aqueous ammonia and agitating to pH9 for 1 hour, when poured into 1000ml distilled water, yellow powder generated. The generated precipitate was filtered, after rinsing, it dried and the 8.1g polymer metal complex was obtained.

[0035] [Example 1] organic electroluminescence devices were produced as follows. 200mg of the copolymer of N-vinylcarbazole compounded in the synthetic example 1 and methacrylic-acid vinyl was dissolved in toluene 5ml, and 10mg of 2 and 2-dimethoxy-2-phenyl acetophenones was added as a photopolymerization initiator, and it dissolved. The spin coat was carried out on the glass with ITO of marketing which carried out washing processing (below 15ohms / **; Central Glass make), the thin film was produced, and it dried under reduced pressure. The photo mask was attached, the thin film which may have irradiated the ultraviolet rays which have the dominant wavelength in 254-365nm was hardened in the shape of [of a photo mask / predetermined] a pattern, and solvent insolubilization was carried out. Next, the thin film which carried out partial hardening was dipped into the toluene solvent, and was etched, and the electron hole transport material layer of the shape of a mask pattern of 50nm of thickness was obtained. Next, 100mg (0.21mmol) of the polymer metal complex (PAA-Sal) Alq2 made as an experiment in the synthetic example 4 was dissolved in chloroform 5ml. This solution was applied with the spin coat method on the electron hole transporting bed, it dried, and the thin film of 110nm of thickness was produced. Next, Mg:Ag=20:1 were produced by 200nm thickness by vapor codeposition as cathode using vacuum-like arrival equipment. In this way, when the seal of approval of the direct current voltage was carried out and luminescence brightness was measured, having set into the fixture which can decompress the produced light emitting device, and decompressing, the brightness of 1300 cd/m2 was obtained by driver voltage 12v.

[0036] [Example 2] organic electroluminescence devices were produced as follows. 200mg of the copolymer of the vinylcarbazole compounded in the synthetic example 1 and methacrylic-acid vinyl was

dissolved in toluene 5ml, and 10mg of 2 and 2-dimethoxy-2-phenyl acetophenones was added as a photopolymerization initiator, and it dissolved, the spin coat was carried out on the glass with ITO of washed marketing (below 15ohms / **; Central Glass make), the thin film was produced, and it dried under reduced pressure. The photo mask was attached, the thin film which the ultraviolet rays which have the dominant wavelength in 254-365nm are irradiated [thin film], and may have had the thin film hardened was hardened in the shape of [of a photo mask / predetermined] a pattern, and solvent insolubilization was carried out. Next, the thin film which carried out partial hardening was dipped into the toluene solvent, and was etched, and the electron hole transport material layer of the shape of a mask pattern of 50nm of thickness was obtained. Next, 100mg (0.32mmol) of 9-n-DESHIRU-3-ethynyl carbazole polymers shown in the synthetic example 2 was dissolved in tetrahydrofuran 5ml, and 8mg (0.1mmol) of tris (2-phenyl pyridine) iridium complexes was added to this solution, it dissolved in it, and the thin film of 25nm of thickness was produced for the solution with the spin coat method on the electron hole transporting bed. Next, using vacuum-like arrival equipment, bathocuproine was produced by 10nm of thickness, and Mg:Ag=20:1 were produced for Alq3 by 200nm thickness by vapor codeposition as 23nm of thickness, and cathode. In this way, when direct current voltage was impressed and luminescence brightness was measured, having set into the fixture which can decompress the produced light emitting device, and decompressing, the brightness of 5500 cd/m2 was obtained by 12v. [0037]

[Effect of the Invention] As explained above, when manufacturing organic electroluminescence devices, the thin film of a substrate was produced using the copolymer of this invention, and the problem of the dissolution of the substrate by the solvent of the organic thin film layer applied by optical exposure from a top hardening and by carrying out solvent insolubilization became that there is nothing. Therefore, the laminating of an organic thin film can be easily performed by repeating and applying the same approach. Moreover, this data means establishment of the technique for carrying out multilayer film production of the organic thin film by the spreading method of profitability, such as a spin coat method, the bar coat method, a dip coating method, the flow coat method, screen printing, and the ink jet printing method, simple high moreover. Furthermore, the film production approach by such spreading method is dramatically advantageous in respect of large-area-izing, lowering of a production cost, workability, etc. to a vacuum deposition method. Furthermore, it is useful invention on industry that efficient organic electroluminescence devices are producible by this approach. It cannot be overemphasized further again that this invention is applicable to all applications that carry out the laminating not only of organic electroluminescence devices but the organic thin film to a multilayer.

[Translation done.]

* NOTICES *

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CLAIMS

[Claim(s)]

[Claim 1] It is the macromolecule electron hole transport material which consists of a copolymer of the vinyl monomer which has a substituent, and the acrylic ester or methacrylic ester which has a partial saturation radical, and is characterized by this substituent being at least one sort chosen from the group of a carbazole radical, a carbazole derivative radical, a triphenylamine radical, and a triphenylamine derivative radical.

[Claim 2] Said partial saturation radical is macromolecule electron hole transport material according to claim 1 characterized by being the aliphatic-unsaturated-hydrocarbon residue whose carbon numbers are 2 thru/or 20.

[Claim 3] The percentage to the whole configuration monomer of the vinyl monomer which has said substituent in said copolymer is macromolecule electron hole transport material according to claim 1 to 2 characterized by being the range of 0.5 thru/or 0.9.

[Claim 4] The polymerization degree of said copolymer is macromolecule transport material according to claim 1 to 3 characterized by being the range of 10 thru/or 100000.

[Claim 5] The organic thin films which are the organic electroluminescence devices possessing the layer which consists of an organic thin film of one or more layers which has a luminous layer at least, and touch between the anode plates and cathode which counter at this luminous layer and/or this luminous layer are organic electroluminescence devices characterized by including macromolecule electron hole transport material according to claim 1 to 4.

[Claim 6] They are the organic electroluminescence devices according to claim 5 characterized by the photoreaction carrying out solvent insolubilization of the thin film with which this electron hole transporting bed consists of macromolecule electron hole transport material according to claim 1 to 4 in the organic electroluminescence devices possessing the electron hole transporting bed and luminous layer which consist of an organic thin film between the anode plates and cathode which counter.

[Claim 7] Said electron hole transporting beds are organic electroluminescence devices according to claim 6 carried out [coming to form the opening pattern configuration of this mask, and] as the description, as a result of carrying out etching clearance of the part in which was covered with the mask which has a predetermined opening pattern, and solvent insolubilization was selectively carried out by the optical exposure, and the part by which the part by which an optical exposure was not carried out, and by which solvent insolubilization is not carried out is formed, and this solvent insolubilization is not carried out with a solvent.

[Translation done.]